ANALYSIS

56(299), November, 2020

ISSN 2278–5469 EISSN 2278–5450

DISCOVERY

An exploratory study and elucidation of the nitrogen content of an Estuary

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Article History

Received: 18 September 2020
Reviewed & Revised: 19/September/2020 *to* 22/October/2020
Accepted: 25 October 2020
Prepared: 27 October 2020
Published: November 2020

Citation

Divya S Rajan. An exploratory study and elucidation of the nitrogen content of an Estuary. *Discovery*, 2020, 56(299), 791-804

Publication License

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General Note

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ABSTRACT

A chain of brackish water systems exists in Kerala. A number of estuaries receive nutrient addition over thousand times than the fertilizer loads added to the agricultural area. The resulting nitrogen and phosphorous inputs leads to elevated phytoplankton productivity, which in turn can lead to eutrophication. United Nations Environment Program has reported that 150 coastal areas worldwide are now starved of oxygen as a result of the decomposition of algal blooms caused by nutrients from agricultural runoff of fertilizers and sewage from cities. Therefore, the assessment of the nutrients inputs is vital for understanding the various biological processes within an estuary. The investigation was planned with the objective of studying the nitrogen content of the upstream and downstream waters of the Thekkumbhagam creek of Ashtamudi estuary's nutrient behavior. The study aimed at identifying the sources, dynamics and sink of nutrient. The amount of nutrients entering this creek is very large and its fate is relevant to water quality management. A comparative increase in the concentration of nutrients is noticed during the monsoon period. The lower concentration of nitrite during the months of April to May might be due to less fresh water input, higher salinity, higher pH and also uptake by phytoplankton. Maximum concentration of nitrate was found in regions where there is the possible

input sources of high nutrient due to waste disposed from the sewage and coconut retting. High nitrate concentration may also lead to animal or fish kills, thus reducing system's productivity. Higher nitrate concentrations increase productivity because algae require nitrate for growth. It is inferred that the concentration of nutrients in the estuary has been regulated by the fresh water flow from Kallada River and also by tidal mixing. The present study thus provides an insight into the nitrate-nitrite fluctuations that reminds us the need for sustaining the pristine nature of the estuary.

Key words
Nitrite, nitrate, physico-chemical, sustaining, denitrification

1. INTRODUCTION

As an 'ecotone' between fresh and marine environments, estuaries generally contain a mixture of fresh water and oceanic species (Arumugan, 2002). The physico-chemical parameter problems have been designed mostly to an excess of nutrients, associated with industrial and municipal waste water, (Balls, 1992) forestry and agriculture (Bell, 1991). The subsequent increase in nutrients loads produces an ecological impact over biological communities (Karlson *et al.,* 2009), associated mostly with eutrophication processes (De Souza, 1999)

Levels of nitrite concentration in estuaries range between 0.5 to 6.0 mg NO2.Nl-1. Nitrite is much more toxic to man and animals than nitrate (Jose, 1999). Together with water movement, these processes of Nitrate occurs naturally in ground water as a result of soil leaching but in areas of high nitrogen fertilizer application it may reach very high levels approximately 500 µgat/l NO3.N). Determination of nitrate plus nitrite in surface water gives a general indication of the nutrient status and levels of organic pollution. Expected nitrate concentration in unpolluted fresh water range from undetectable levels to 10 mg/l (Wetzel, 1983). Natural level of nitrate reported in most estuarine water ranges from 10 to 40 µgat/l and decreases to very low values in the marine end (De Souza *et al*., 1981). Nitrate is a major inorganic nutrient that drives primary production in aquatic habitats. Therefore nitrate analysis help to explain ecosystem dynamics. However high concentration may also lead to animal or fish kills, thus reducing system productivity.

To characterize the estuarine environment - general features, distribution pattern of various pollutants, salinity intrusion, abundance of nutrients etc. The main factors influencing the hydrographic conditions of an estuary are the saline water intrusion associated with tides and the freshwater brought in by the rivers. Hydrographic feature such as temperature, pH, flow patterns, Dissolved Oxygen, Biological Oxygen Demand, salinity, nutrients etc are generally influenced by the topographic as well as climatic conditions. Estuarine systems play important roles in the exchange of materials nutrients, carbon) etc. Hydrographic features show wide variations from estuary to estuary and hence every estuary is unique. Thus hydrological and ecological studies of estuaries are important as these regions are fertile and are the most productive ecosystems of the planet (Jose 1993).The present chapter analyses the status of nutrients in the estuary in relation with other physico-chemical parameters. This estuarine system is largely influenced by the influx of fresh water, which in turn is controlled by the monsoon spell. The given investigation identifies the nitrogen flux within the estuary.

2. MATERIALS AND METHODS

Monthly water samples for hydrographical studies have been made from four selected sites of Thekkumbhagam creek of Ashtamudi estuary in Kollam district for a period of two years (From June 2008 to May 2010), covering three prominent seasons of the year (pre-monsoon, monsoon and post-monsoon). All collections were made invariably between 6 am and 8 am. Surface and bottom water samples were taken in good quality polyethylene containers for the analysis of certain physico-chemical factors. Maximum care was taken in taking samples, their preservatives, storage and analysis. The samples were brought to the laboratory immediately after collection, for analyzing its various physico-chemical characteristics using standard methods. Nitrite nitrogen was determined spectrophotometrically at 543nm with sodium nitrite solution as standard (Parson *et al.* 1984).The data collected at monthly intervals from all the stations were statistically analysed, with a view to understand the nature of variations in the physico-chemical parameters between stations and seasons. Analysis includes Mean, Standard Deviation, ANOVA.

3. RESULTS

Nitrite Nitrogen (µg NO2.N/l)

In Station 1, the nitrite of surface water ranged from 0 to 1665 µg NO2.N/l in 2008-2009 and from 0 to 1998 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon, pre-monsoon were 333 ± 135.95, 416.25 ± 159.41,582.75 ± 369.19

respectively in the first year and 333 ± 135.95, 416.25 ± 159.41,749.25 ± 437.89 respectively in the second year. The annual mean ± SE was 444 ±131.76 in 2008-2009 and 499.5 ± 156.08 in 2009-2010(Table 1.1 & 1.3, 1.4 and Fig 1.1a & 1.1b). In Station 1, the Nitrite of bottom water ranged from 0 to 1666 µgNO2.N/l in 2008-2009 and from 0 to 999 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon, pre-monsoon were 333 ± 192.26, 582.75 ± 209.51,583 ± 369.43 respectively in the first year and 249.75 ± 159.41, 416.25 ± 209.51, 333 ± 135.95 respectively in the second year. The annual mean ± SE was 499.58 ± 144.98 in 2008-2009 and 333 ± 91.66 in 2009-2010 (Table 1.1 & 1.3,1.4 and Fig 1.1a & 1.1b).

In Station 2, the nitrite of surface water ranged from 0 to 4666 µg NO2.N/l in 2008-2009 and from 0 to 4950 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 1146.25 ± 1091.75, 1165.5 ± 552.22, and 166.5 ± 96.13 respectively in the first year and 1487.25 ± 1162.23, 1323 ± 402.53, 660 ± 660 respectively in the second year. The annual mean ± SE was 916.08 ± 444.24 in 2008-2009 and 1156.75 ± 434.46 in 2009-2010 (Table 1.1 & 1.3, 1.4 and Fig 1.1a & 1.1b).

In Station 2, the Nitrite of bottom water ranged from 0 to 2997 µg NO2.N/l in 2008-2009 and from 0 to 2970 µg NO2.N/l in 2009-2010. The mean monsoon, post-monsoon and pre-monsoon were 416.25 ± 159.41, 1332 ±560.52, and 416.25 ± 159.41 respectively in the first year and 333 ± 135.95, 1242 ±591.83, 909 ± 691.47 respectively in the second year. The annual mean ± SE was721.5 ± 223.88 in 2008-2009 and 828 ± 299.68 in 2009-2010(Table 1.1 & 1.5, 1.6 and Fig 1.2 a & 1.2b).

In Station 3, the nitrite of surface water ranged from 333 to 1332 µgNO2.N/l in 2008-2009 and from 0 to 1665 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 582.75 ± 249.75, 666 ±192.26, and 749.25 ± 159.41 respectively in the first year and 531.63 ± 383.96, 749.25± 209.51, 582.75 ± 83.25 respectively in the second year. The annual mean ± SE was832.5 ± 214.95, and 333 ± 135.95 respectively in the first year and 4291.5 ± 4072.53, 915.75 ± 83.25, 416.25 ± 159.41 respectively in the second year (Table 1.1 & 1.3, 1.4 and Fig 1.1a & 1.1b).

In Station 4, the Nitrite of bottom water ranged from 333 to 4000 µgNO2.N/l in 2008-2009 and from 333 to 4620 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 2333 ± 172, 832.5 ±214.95, and 249.75 ± 159.47 respectively in the first year and 4987.5 ± 941.84, 499.5± 96.13, 662.25 ± 404.78 respectively in the second year. The annual mean ± SE was 1138.42 ± 1403 in 2008-2009 and 1049.75 ± 369.79 in 2009-2010 (Table 1.1 & 1.5,1.6 and Fig 1.2 a & 1.2b).

ANOVA comparing the nitrite of surface water between estuary's stations showed no significant variations for 2008-2009 and 2009-2010. ANOVA comparing nitrite surface values between the years of study showed variations between seasons, periods within seasons significant at 1% level for station 1. In the case of station 2, it showed variation between years, significant at 1% and between seasons significant at 5% level. Station 3 and 4 showed variations between years significant at 1% level (Table 1.3 & 1.4). ANOVA showed no significant variation on comparison between stations during 2008-2009 and 2009-2010. ANOVA comparing variations between years of study, station 1 showed no significant variation but station 2 and station 3 showed variations between years significant at 1% level. Station 4 showed variations between years significant at 1% level and between seasons significant at 5% level (Table 1.5 & 1.6).

Table 1.1 Nitrite (µg NO_2.N/l) of water (2008-2010)

Year	Season	Month	Nitrite (µg NO_2.N/l)							
			Station 1		Station 2		Station 3		Station 4	
			Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
2008-2009	Monsoon	JUN	333	0	333	0	333	1000	18000	4000
		JUL	666	666	4666	666	333	666	16666	4000
		AUG	333	0	0	333	1332	335	0	333
		SEP	0	666	666	666	333	666	0	999
	Post-Monsoon	OCT	666	666	333	666	333	666	999	666
		NOV	666	999	333	999	333	333	333	1332

		DEC	333	0	2664	2997	999	666	1332	999
		JAN	0	666	1332	666	999	1332	666	333
	Pre-Monsoon	**FEB**	333	333	333	666	999	333	333	0
		MAR	1665	1666	0	0	999	1332	0	0
		APR	0	0	0	333	666	666	333	333
		MAY	333	333	333	666	333	333	666	666
2009-2010	**Monsoon**	**JUN**	333	0	333	0	0	666	16500	4620
		JUL	333	333	4950	333	128.5	333	666	1998
		AUG	666	0	0	333	1665	0	0	333
		SEP	0	666	666	666	333	666	0	999
	Post-Monsoon	**OCT**	333	333	666	333	666	333	666	333
		NOV	666	333	666	666	333	999	999	666
		DEC	666	0	2310	2970	1332	666	999	666
		JAN	0	999	1650	999	666	1332	999	333
	Pre-Monsoon	**FEB**	666	666	2640	2970	666	999	666	999
		MAR	1998	333	0	0	666	1650	0	0
		APR	0	0	0	333	333	333	333	0
		MAY	333	333	0	333	666	666	666	1650

Table 1.2 Nitrate (µg NO_3.N/l) of water (2008-2010)

Year	**Season**	**Month**	**Nitrate (µg NO_3.N/l)**							
			Station 1		**Station 2**		**Station 3**		**Station 4**	
			Surface	**Bottom**	**Surface**	**Bottom**	**Surface**	**Bottom**	**Surface**	**Bottom**
2008-2009	**Monsoon**	**JUN**	480	480	627	700	250.3	667	10000	8800
		JUL	800	640	3546	346	787	346	16026	3333
		AUG	960	480	960	467	212	947	960	787
		SEP	1120	160	614	500	173	316	320	519

	Post-Monsoon	OCT	320	320	467	134	627	26	199	186
		NOV	4160	480	147	519	147	307	787	852
		DEC	320	480	2184	2357	679	26	52	359
		JAN	640	960	532	294	199	372	294	467
	Pre-Monsoon	FEB	320	320	13	346	679	13	13	0
		MAR	1120	800	800	480	679	692	480	320
		APR	160	640	160	147	26	294	467	13
		MAY	320	640	13	26	147	467	294	26
2009-2010	Monsoon	JUN	307	640	467	640	960	186	11700	2580
		JUL	627	467	2550	467	960	173	26	718
		AUG	614	640	1120	627	385	1440	1120	947
		SEP	1120	506	614	506	249.7	26	320	359
	Post-Monsoon	OCT	147	307	26	332.8	457	467	26	147
		NOV	774	307	134	26	467	39	39	346
		DEC	186	320	1030	1530	532	294	281	134
		JAN	640	39	690	199	26	532	121	306.2
	Pre-Monsoon	FEB	186	186	2320	2650	186	519	186	999
		MAR	718	627	960	320	346	1170	320	160
		APR	320	800	160	166.5	307	467	147	800
		MAY	147	307	160	147	307	294	26	690

Table 1.3 ANOVA testing Nitrite of Surface water between the stations and seasons

	2008-2009			2009-2010		
Source	**Sum of squares**	**Mean Sum of squares**	**F Ratio**	**Sum of squares**	**Mean Sum of squares**	**F Ratio**
Total	564542100.00			279708300.00		
Between stations	62271090.00	20757030.00	1.90	14130380.00	4710126.00	0.70
Between seasons	49430650.00	24715320.00	2.29	9806744.00	4903372.00	0.76
Periods within seasons	97006284.00	10778476.00	1.00	43863678.00	4873742.00	0.76
Error	355689700.00	10778476.00		211907500.00	6421439.40	

Table 1.4 ANOVA testing Nitrite of surface water between the years of study in stations

	Station 1			Station 2		
Source	**Sum of squares**	**Mean Sum of squares**	**F**	**Sum of squares**	**Mean Sum of squares**	**F**
Total	5525969.00			48.00		
Between years	18481.50	18481.50	0.60	8.20	8.20	10.2**
Between seasons	480519.00	240259.50	8.41**	10.70	5.30	6.65*
Periods within seasons	4712783.00	523642.50	18.33**	20.31	2.26	2.81
Error	314185.50	28562.32		8.83	0.80	

	Station 3			Station 4		
Source	**Sum of squares**	**Mean Sum of squares**	**F**	**Sum of squares**	**Mean Sum of squares**	**F**
Total	79.60			91.70		
Between years	40.00	40.00	31.6**	47.30	47.30	23**
Between seasons	1.80	0.90	0.69	3.10	1.50	0.74
Periods within seasons	23.88	2.65	2.09	18.62	2.07	1.00
Error	13.96	1.27		22.67	2.06	

*** denote significance ($p < .05$)**

**** denote significance ($p < .01$)**

Table 1.5 ANOVA testing Nitrite of bottom water between the stations and seasons

	2008-2009				2009-2010			
Source	**DF**	**Sum of squares**	**Mean Sum of squares**	**F Ratio**	**DF**	**Sum of squares**	**Mean Sum of squares**	**F Ratio**
Total	47	34862220.00			47	36622920.00		
Between stations	3	2601704.00	867234.70	1.10	3	3234214.00	1078071.0 0	1.40
Between seasons	2	1976154.00	988077.00	2.18	2	19758.00	9879.00	0.01
Periods within seasons	9	4732056.00	525784.00	0.68	9	7246802.00	805200.30	1.02
Error	33	25552300.00	774312.12		33	26122150.00	791580.30	

Table 1.6 ANOVA testing Nitrite of bottom water between the years of study in stations

	Station 1				Station 2			
Source	**DF**	**Sum of squares**	**Mean Sum of squares**	**F Ratio**	**DF**	**Sum of squares**	**Mean Sum of squares**	**F Ratio**
Total	23	4049947.00			23	2428.60		
Between years	1	166500.00	166500.00	1.60	1	2408.40	2408.40	2215**
Between seasons	2	194139.00	97069.50	0.92	2	2.80	1.40	1.28
Periods within	9	2523808.00	280423.10	2.65	9	5.41	0.60	0.55

seasons								
Error	11	1165501.00	105954.60		11	11.96	1.09	

	Station 3				Station 4			
Source	DF	Sum of squares	Mean Sum of squares	F Ratio	DF	Sum of squares	Mean Sum of squares	F Ratio
Total	23	2467.30			23	2682.20		
Between years	1	2444.00	2444.00	2638.3**	1	2665.10	2665.10	4630.2**
Between seasons	2	2.60	1.30	1.38	2	5.00	2.50	4.32*
Periods within seasons	9	10.51	1.17	1.26	9	5.73	0.64	1.11
Error	11	10.19	0.93		11	6.30	0.58	

*** denote significance ($p < .05$)**

**** denote significance ($p < .01$)**

Table 1.7 ANOVA testing Nitrate of surface water between the stations and seasons

	2008-2009			2009-2010		
Source	Sum of squares	Mean Sum of squares	F	Sum of squares	Mean Sum of squares	F Ratio
Total	340767200.00			135457900.00		
Between stations	30578730.00	10192910.00	1.60	4547890.00	1515963.00	0.50
Between seasons	36463550.00	18231770.00	2.83	12022680.00	6011338.00	2.03
Periods within seasons	61449075.00	6827675.00	1.06	21051900.00	2339100.08	0.79
Error	212275900.00	6432603.00		97835390.00	2964708.80	

Table 1.8 ANOVA testing Nitrate of surface water between the years of study in stations

	Station 1			Station 2		
Source	Sum of squares	Mean Sum of squares	F	Sum of squares	Mean Sum of squares	F
Total	14956980.00			406.50		
Between years	1014347.00	1014347.00	2.30	262.70	262.70	40.3**
Between seasons	1000552.00	500276.00	1.11	30.60	15.30	2.35
Periods within seasons	7992658.00	888073.00	1.97	41.63	4.63	0.71
Error	4949421.00	449947.40		71.63	6.51	

	Station 3			Station 4		
Source	Sum of squares	Mean Sum of squares	F	Sum of squares	Mean Sum of squares	F
Total	601.20			1214.90		
Between years	135.80	135.80	6.6*	338.60	338.60	8.4*
Between seasons	94.10	47.00	2.28	135.70	67.80	1.68
Periods within seasons	144.58	16.07	0.78	295.37	32.82	0.81

Error	226.75	20.61		445.25	40.48	

*** denote significance (p < .05)**

**** denote significance (p < .01)**

Table 1.9 ANOVA testing Nitrate of bottom water between the stations and seasons

	2008-2009			2009-2010		
Source	**Sum of squares**	**Mean Sum of squares**	**F Ratio**	**Sum of squares**	**Mean Sum of squares**	**F Ratio**
Total	82065860.00			14265720.00		
Between stations	6363398.00	2121133.00	1.30	552771.00	184257.00	6**
Between seasons	7099140.00	3549570.00	2.13	1176344.00	588172.00	1.99
Periods within seasons	13582890.00	1509210.00	0.91	2797010.00	310778.90	1.05
Error	55020420.00	1667285.50		9739597.00	295139.30	

Table 1.10 ANOVA testing Nitrate of bottom water between the years of study in stations

	Station 1			Station 2		
Source	**Sum of squares**	**Mean Sum of squares**	**F**	**Sum of squares**	**Mean Sum of squares**	**F**
Total	1135530.00			1190.20		
Between years	65521.50	65521.50	1.20	845.00	845.00	40.7**
Between seasons	81654.00	40827.00	0.78	16.80	8.40	0.40
Periods within seasons	409297.00	45477.45	0.86	99.83	11.09	0.53
Error	579057.50	52641.59		228.53	20.78	

	Station 3			Station 4		
Source	**Sum of squares**	**Mean Sum of squares**	**F**	**Sum of squares**	**Mean Sum of squares**	**F**
Total	800.00			1609.40		
Between years	494.50	494.50	30.5**	1128.20	1128.20	51.4**
Between seasons	55.30	27.60	1.71	95.70	47.90	2.18
Periods within seasons	72.06	8.01	0.49	143.93	15.99	0.73
Error	178.16	16.20		241.58	21.96	

*** denote significance (p < .05)**

**** denote significance (p < .01)**

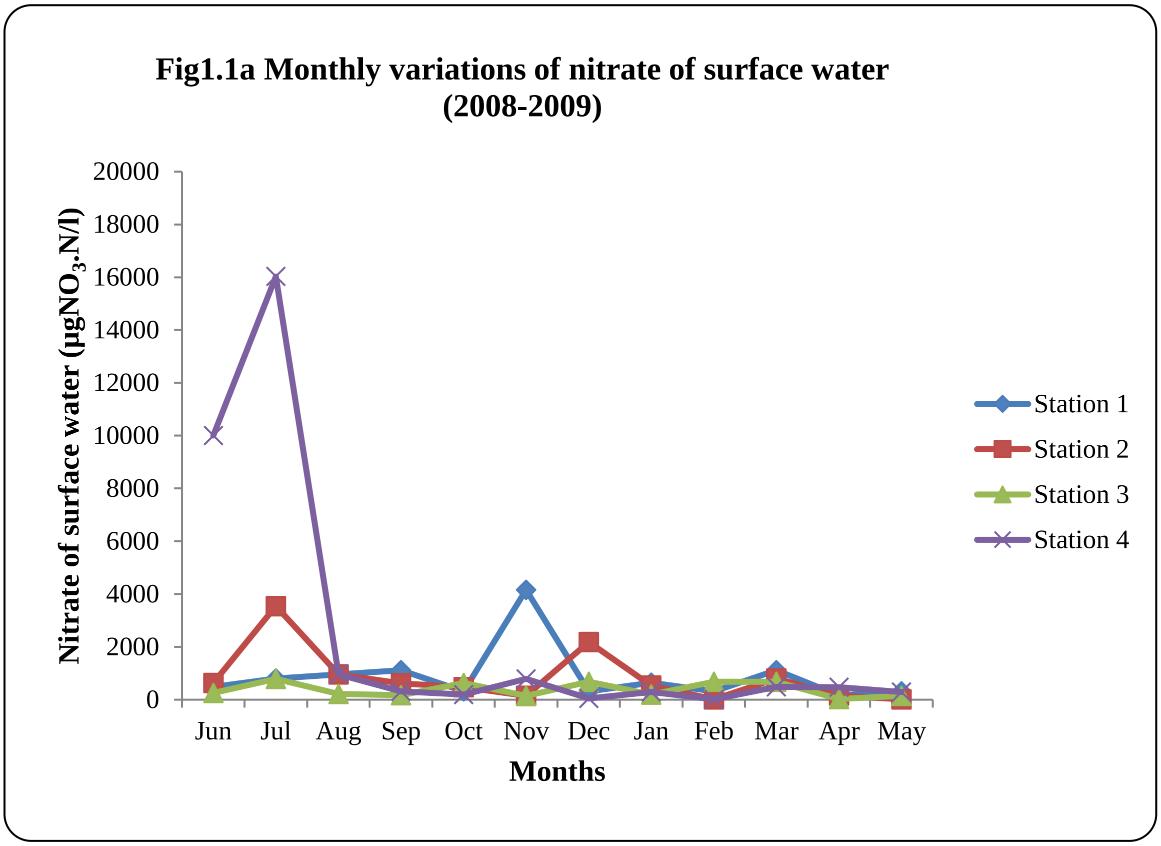


Fig1.1a Monthly variations of nitrate of surface water
(2008-2009)
Nitrate of surface water (µgNO3.N/l)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May
Months
Station 1
Station 2
Station 3
Station 4

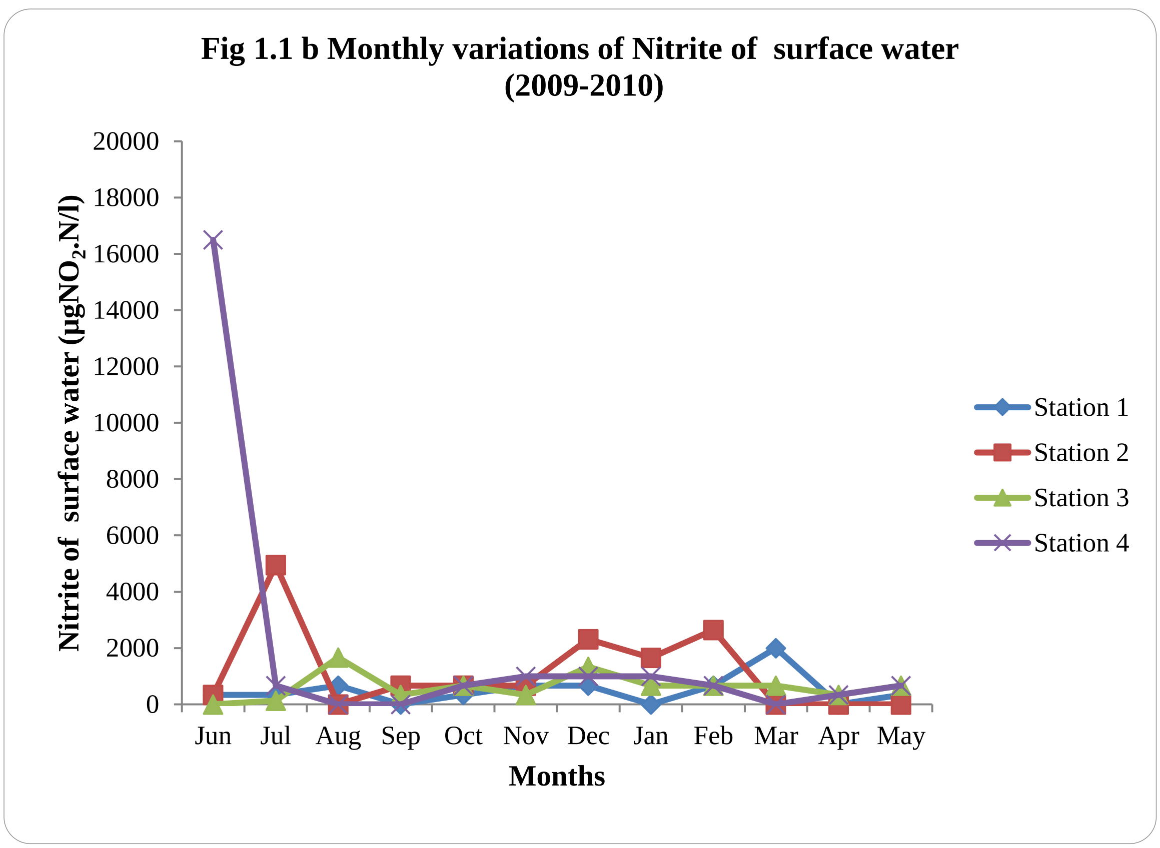


Fig 1.1 b Monthly variations of Nitrite of surface water
(2009-2010)
Nitrite of surface water (µgNO2.N/l)
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
Jun Jul Aug Sep Oct Nov Dec Jan Feb Mar Apr May
Months
Station 1
Station 2
Station 3
Station 4

Fig 1.2a Monthly variations of nitrite of bottom water (2008-2009)

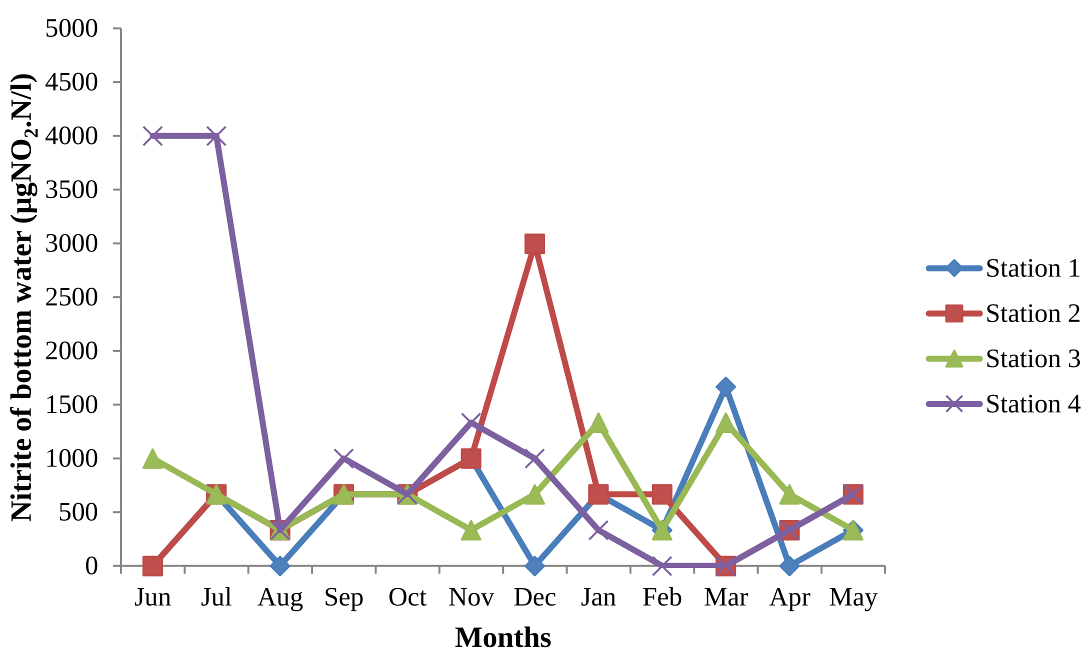
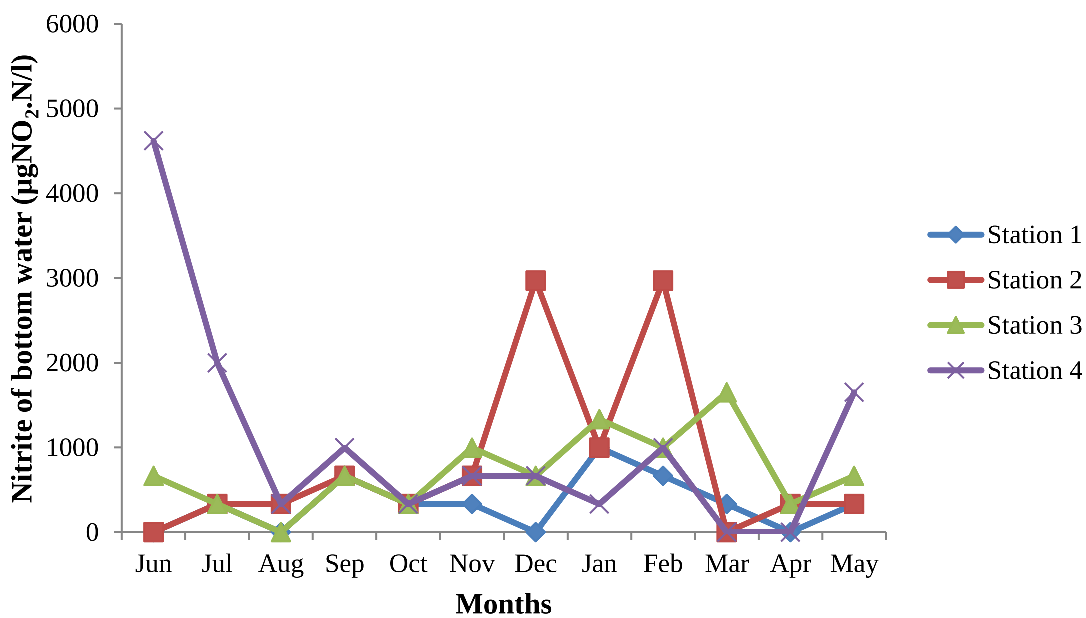


Fig 1.2b Monthly variations of nitrite of bottom water (2009-2010)



Nitrate Nitrogen (µg NO3.N/l)

In Station 1, the nitrate of surface water ranged from 160 µg to 4160 µgNO2.N/l in 2008-2009 and from 147 to 1120 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon, pre-monsoon were 840 ± 136.63, 1360 ± 936.38, 480 ± 216.64 respectively in the first year and 667 ± 168.13, 436.75 ± 158.61, 666 ± 108.45 in 2008-2009 and 621.21 ± 137.14 in 2009-2010(Table 1.2 & 1.7,1.8 and Fig 1.2 a & 1.2 b).

In Station 3, the Nitrite of bottom water ranged from 333 to 1332 µgNO2.N/l in 2008-2009 and from 333 to 1665 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 666.75 ± 135.74, 749.25 ± 209.51, and 666 ± 235.47 respectively in the first year and 416.25 ± 159.41, 832.25 ± 214.95, 912 ± 281.06 respectively in the second year. The annual mean ± SE was 694 ± 104.14 in 2008-2009 and 720.25 ± 134.12 in 2009-2010(Table 1.2 & 1.9,1.10 and Fig1.2 a & 1.2 b).

In Station 4, the nitrite of surface water ranged from 0 to 18000 µg NO2.N/l in 2008-2009 and from 0 to 16500 µg NO2.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 8666.5 ± 5011.01, 342.75 ± 130.45 respectively in the second year. The annual mean ± SE was 893.33 ±312.31 in 2008-2009 and 482.17 ± 89.95 in 2009-2010 . (Table 1.2 & 1.7,1.8 and Fig 1.2 a & 1.2 b).

In Station 1, the nitrate of bottom water ranged from 160 µg to 960 µgNO3.N/l in 2008-2009 and from 39 to 800 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon, pre-monsoon were 440 ± 100.66, 560 ± 138.56, 600 ± 100.66 respectively in the first year and 563.25 ± 45.02, 243.25 ± 68.15, 480 ± 141.53 respectively in the second year. The annual mean ± SE was 533.33 ± 63.31 in 2008-2009 and 428.83 ± 64.02 in 2009-2010. (Table 1.2 & 1.9,1.10 and Fig1.2 a & 1.2 b).

In Station 2, the nitrate of surface water ranged from 13 to 3546 µg NO3.N/l in 2008-2009 and from 26 to 2550 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 1436.75 ± 707.63, 832.5 ± 458.29, and 246.5 ± 187.73 respectively in the first year and 1187.75 ± 475.13, 470 ± 236.65, 900 ± 509.51 respectively in the second year. The annual mean ± SE was 838.58 ± 298.81 in 2008-2009 and 852.58 ± 239 in 2009-2010. (Table 1.2 & 1.7,1.8 and Fig 1.2 a & 1.2 b).

In Station 2, the nitrate of bottom water ranged from 26 to 2357 µgNO3.N/l in 2008-2009 and from 26 to 2650 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 503.25 ± 73.46, 826 ± 516.41, and 249.75 ± 101.2 respectively in the first year and 560 ± 43.26, 521.95 ± 341.89, 820.88 ± 610.93 respectively in the second year. The annual mean ± SE was 526.33 ± 175.27 in 2008-2009 and 634.28 ± 215.25 in 2009-2010. (Table 1.2 & 1.9,1.10 and Fig1.2 a & 1.2 b).

In Station 3, the nitrate of surface water ranged from 26 to 787 µg NO3.N/l in 2008-2009 and from 26 to 2320 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 355.58 ± 144.67, 413 ± 139.37, and 382.75 ± 172.81 respectively in the first year and 638.68 ± 187.56, 370.5 ± 116.03, 286.5 ± 34.74 respectively in the second year. The annual mean ± SE was 383.78 ± 80.21 in 2008-2009 and 431.89 ± 81.13 in 2009-2010(Table 1.2 & 1.7,1.8 and Fig 1.2 a & 1.2 b)..

In Station 3, the nitrate of bottom water ranged from 26 to 947 µg NO3.N/l in 2008-2009 and from 26 to 1170 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 569.75 ± 148.95, 182.75 ± 91.47, and 366.5 ± 143.26 respectively in the first year and 456.25 ± 329.92, 333 ± 110.12, 612.5 ± 191.96 respectively in the second year. The annual mean ± SE was 372.75 ± 83.09 in 2008-2009 and 467.25 ± 124.64 in 2009-2010. (Table 1.2 & 1.9, 1.10 and Fig1.2 a & 1.2 b).

In Station 4, the nitrate of surface water ranged from 13 to 16300 µg NO3.N/l in 2008-2009 and from 26 to 11700 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 6826.5 ± 3779.91, 333 ± 159.31, and 313.5 ± 108.77 respectively in the first year and 3291.5 ± 2812.35, 116.75 ± 58.65, 169.75 ± 60.57 respectively in the second year. The annual mean ± SE was 2491 ± 1468.56 in 2008-2009 and 1192.67 ± 959.14 in 2009-2010. (Table 1.2 & 1.7,1.8 and Fig 1.2 a & 1.2 b).

In Station 4, the nitrate of bottom water ranged from 0 to 8800 µg NO3.N/l in 2008-2009 and from 134 to 2580 µg NO3.N/l in 2009-2010. The mean values during monsoon, post-monsoon and pre-monsoon were 3359.75 ± 1921.07, 466 ± 141.08, and 89.75 ± 76.93 respectively in the first year and 1151 ± 491.46, 233.33 ± 54.26, 662.25 ± 179.21 respectively in the second year. The annual mean ± SE was 1305.17 ± 729.09 in 2008-2009 and 682.18 ± 194.74 in 2009-2010. (Table 1.2 & 1.9,1.10 and Fig1.2 a & 1.2 b).

ANOVA comparing nitrate of surface water of 2008-2009, 2009-2010 between estuary stations showed no significant variations. ANOVA comparing nitrate of surface water values between the years of study revealed no significant variations for station 1. But station 2 showed variations between years significant at 1% level. In the case of station 3 and station 4 showed variations between years significant at 5% level (Table 1.7,1.8). ANOVA comparing nitrate of bottom water values showed no significant variations between stations for both years. But on comparison with the years of study station 2, 3,4 showed variations between years at 1% level while station 1 showed no significant variations(Table 1.9 &1.10).

4. DISCUSSION

Nitrite Nitrogen

The nitrite ion is the common form of combined nitrogen found in natural water. High nitrite concentration is generally indicative of industrial effluents and is often associated with unsatisfactory microbiological quality of water.

The present study recorded nitrite nitrogen of surface water from 0 to18000 µgNO2.N /l and nitrite of bottom water ranges from 0 to 4000 µgNO2.N /l in 2008-2009. Nitrite surface range from 0 to 16500 µgNO2.N /l and nitrite bottom ranged from 0 to 4620 µgNO2.N /l in 2009-2010.A comparative increase in the concentration of nutrients is noticed during the monsoon period. This may be due to the Kallada river flow, heavy rainfall, land drainage, input of fertilizers etc. There is also the direct discharge of organic waste in addition to the industrial wastes. The inputs of coconut husks from retting grounds, fishery waste from fish processing industry were also common. By the decomposition of organic waste nitrate has been formed. This was in conformation with the findings of Satpathy (1996). Previous research studies of Nair *et al.,* (1983a,b) on Ashtamudi also commented about the heavy river flow of Kallada River which dilutes the industrial effluents. Nitrite concentration in some months was found to be lower than nitrate probably. Peak values of nitrite during the monsoon season (Mitra *et al.,* 1998). Further excretion of phytoplankton reduction of nitrate and oxidation of ammonia all contribute together individually for an increase in the concentration of nitrite in the environment. Similar reports were given by Jose (1993).

Low values of nitrite observed during the summer season might be due to the lesser amount of fresh water inflow and higher salinity. Similar findings were earlier given by Satpathy (1996) from coastal water of Kalpakkam; Prabhu *et al.*,(2000) from Pichavaram mangroves; Sundaramanickam *et al.,* (2008) from Parangipettai and Cuddalore coast and Damotharan *et al.,*(2010) from Point Calimere coastal waters, India. Discharge of industrial effluents or nitrite containing effluents from sewage plant may cause an increase in the concentration levels of nitrite which can eventually affect the water quality. Nitrite is much more toxic to man and animals than nitrate. Sarala Devi *et al.,* (1983) reported nitrite concentration of some estuaries in Kerala ranging between 0.05 to 2.16 µg at NO2.N l-1. Several investigations have reported that nitrogen acts as the limiting nutrient to primary productivity in marine and estuarine systems (Nixon, 1986). So the primary productivity of an estuary depends on the effectiveness of regenerating nitrogen in the required form on a rapid time scale and the supply of new nitrogenfrom marine and riverine sources (Aston, 1980). Nitrite content was also found to be high in some months in the lower reaches than the upper reaches and which could be attributed to the variation in phytoplankton excretion and oxidation of ammonia and reduction of nitrite (Kannan, 1996). The lower concentration of nitrite during the months of April to May might be due to less fresh water input, higher salinity, higher pH and also uptake by phytoplankton. The same was recorded by Chandran (1982); Shekar (1987); from Kolhadarn estuary Sivakumar (1982) from Vellar estuary and Mathevan Pillai (1994) from Cuddalore Uppanar estuary. In the case of station 2 and station 3 mean values of post-monsoon were found to be maximum. Here nitrite concentration was significantly high only in the post-monsoon season. The nitrifying bacteria can play a key role as they are able to oxidize ammonium to nitrate with nitrite as an intermediate. Nitrite may also be formed in the reduction of nitrate and denitrification.

Nitrate Nitrogen

The role of nitrogen in estuarine water quality and in maintaining and enhancing estuarine productivity has stimulated the study of various forms of this in estuarine ecology. Nitrogen supplied through rivers mainly exists as dissolved nitrate, which is derived from rock weathering and drainage from agricultural lands. Nitrate is considered as the stable oxidation level of nitrogen in sea water (Grasshoff *et al.*,, 1983). Nitrate is the common form of Nitrogen found in natural water and is changed by biochemical process to nitrite when there is no oxygen. When oxygen is present the nitrite quickly forms nitrate.

Nitrite produces carcinogenic nitrosamines in the human body through its reaction with amines or amides (Badiaka and Kenchaiah, 2009). Nitrite is thus one of the pollutants found in the atmosphere and natural water and is an important intermediate in biological nitrogen cycle (Belzunce *et al.*, 2004). Thus discharge of industrial effluents or nitrite containing effluents from sewage plant may cause increase in the concentration levels of nitrite which can eventually affect the water quality. Thus monitoring of nitrite concentration in estuarine forms a relevant tool in water quality monitoring. A major inorganic nutrient that drives primary production in aquatic habitats is Nitrate (NO3-) therefore nitrate analysis helps to explain ecosystem dynamics. Natural level of nitrate reported in most estuarine waters range from 10 to 40 µg at / l and decreases to very low values in the marine end (,Sharp, 1986). The nitrate of surface water values ranged from 13 to 16026 µg NO3.N/l and nitrate of bottom water ranged from 0 to 8800 µg NO3.N/l in 2008-2009. The nitrate surface values ranges from 26 to 11700 µg NO3.N/l and nitrate bottom value ranges from 26 to 2580 µg NO3.N/l. An increase in the nitrate content upto10390µgNO3.N was reported in river Chitrapuzha by Babu (2000). This agrees with the findings of the present study showing that the higher nitrate values indicated the external addition of some effluents rich in nitrogenous compounds during the period of study causing degradation of water quality.

Maximum concentration of nitrate was found in regions where there is the possible input sources of high nutrient due to waste disposed from the sewage and coconut retting. Higher nitrate values were reported earlier from the severely polluted areas of Ashtamudi estuary (Nair *et al.,* 1984) and Adayar mangroves waters (Selvam *et al.,* 1994) due to decomposition of organic matter. High values in some stations maybe due to sewage pollution Station 4 is a more polluted one with direct discharge of organic wastes, in addition to the discharges of industrial wastes, the input from the nearly coconut husk retting grounds and dumping of fishery, poultry, slaughter wastes etc. The highest nitrate level is due to the fresh water inflow; litter fall decomposition and terrestrial run off during the monsoon/ post-monsoon seasons another possible way of nitrate entry is through oxidation of NH3 form of nitrogen to nitrite formation. Similar findings agree with the reports of, Rajasegar (2003). The low value recorded during pre-monsoon period may be due to its utilization by phytoplankton as evidenced by high photosynthetic activity. High nitrate concentration may also lead to animal or fish kills, thus reducing system's productivity. Higher nitrate concentrations increase productivity because algae require nitrate for growth. It is inferred that the concentration of nutrients in the estuary has been regulated by the fresh water flow from Kallada River and also by tidal mixing. In the non-monsoon season there is only a reduced fresh water flow from Kallada River together with the addition of contaminants in large quantities which lead to the depletion of dissolved oxygen and subsequent non oxidation of organic matter. The study points out a higher concentration of nitrate. Because high nitrate concentration is toxic, the Environmental Protection Agency determined that the maximum concentration limit for nitrate in water is 10 parts per million (ppm). The present study indicates a nitrate concentration above the permissible limits.

5. CONCLUSION

Nitrogen is essential for living organisms as an important constituent of proteins, including genetic material. In the environment, inorganic nitrogen occurs in a range of oxidation states as nitrate (NO3) and nitrite (N02), the ammonium ion (NH4+) and molecular nitrogen (N2). It undergoes biological and non-biological transformation in the environment as part of the nitrogen cycle. Heavy rainfall and consequent land drainage, sewage deposition was observed to be the main source of nitrate in the estuary. High nitrate concentration in the runoff waters can be related to the large amount of nitrogenous fertilizers used in agriculture. The concentrations of various forms of nitrogen in an estuary at a given time is controlled by factors like input rates, the incoming tides, the inter-conversion reactions occurring in the water column, fresh water discharges, denitrification, deposition etc. Anthropogenic sources add considerable contribution of nitrate ions. Human and animal waste, fertilizers and other industrial waste can contribute substantial amount of nitrate ions in to the aquatic system. Since high nitrate ions concentration affects the oxygen carrying capacity of blood an upper limit of 10 mgNO3.N/l is recommended by most authorities. The present evaluation thus provides an insight into the nitrate-nitrite fluctuations that reminds us the need for conserving the estuary.

ACKNOWLEDGEMENT

The author is extremely grateful to the PG and Research department of Zoology of Sree Narayana College, Kollam for the facility rendered during the tenure work.

Funding

This research did not receive any funding.

Conflict of Interest

The authors declare no conflicts of interests any matter related to this paper.

Data and materials availability

All related data have been presented in this paper.

Peer-review

External peer-review was done through double-blind method.

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